OBSERVATIONS ON THE 8-HYDROXYQUINOLINE AND RELATED DERIVATIVES OF GALLIUM, INDIUM AND THALLIUM

BY

ALVIN JEROME COHEN

B.S., University of Florida, 1940

AN ABSTRACT OF A THESIS

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Introduction

Oxine (8-hydroxyquinoline) reacts with a large number of metal ions to form insoluble, colored, chelate compounds. It is probable that the metal oxinates (8-hydroxyquinolates) are derived from the enol form of the reagent. In general, the number of oxine groups in the molecule is numerically equal to the valence of the metal.

The oxinates (and derivatives) of the IIIB family were chosen for study because of the renewed interest in the chemistry of gallium and related elements. Since the aluminum and indium compounds have been studied extensively and their absorption spectra investigated (3), these materials were included in only a comparative way, and attention was directed primarily to the gallium and thallium compounds.

Special emphasis was placed on the comparative spectrophotometric investigations of the IIIB family oxinates in chloroform solutions. This work was undertaken with the purpose of showing relationships and trends in this family as reflected by the chemistry and absorption spectra of the oxinates.

Trends in the family were observed with respect to the pH of oxinate precipitation, pH range of maximum extraction by oxine in chloroform, wave lengths and molecular extinctions of the absorption peaks, stability of the oxinates in chloroform solution, adherence to Beer's Law and applicability of the compounds to analytical practice.

Experimental And Discussion

Gallium forms a well-characterized oxinate, the composi-

tion of which closely approximates that given by the formula, $Ga(C_9H_6NO)_3$ (2). This compound begins to precipitate from solution at an average pH of 2.82 (75° C.) and the precipitation appears to be complete at a pH of 3.10. Gallium oxinate has been proposed for the gravimetric determination of small amounts of gallium (2). The oxine chelated to the gallium may be determined by bromate titration and the gallium content of the compound calculated from this.

The absorption spectra of solutions of gallium in chloroform were investigated by means of an unmodified Beckman Model DU Quartz Spectrophotometer (used throughout this work). All solutions observed were placed in 5.0 cm. demountable absorption cells with quartz windows. In the wave length range 252-600 mμ, four absorption peaks were observed at 254-268, 320, 335 and 392.5 mμ. The last three peaks were found to obey Beer's Law, and the 392.5 mμ peak was found suitable for use in colorimetric procedures within the concentration range 0.1-2.5 mg. of gallium (as the metal) per liter of chloroform.

The extraction of gallium from aqueous solutions was investigated by using oxine in chloroform as the extracting agent. The extraction of the metal was found to be complete in the pH region, 3.0-6.2 under the conditions outlined. This extraction procedure makes possible a direct colorimetric estimation of the gallium present in an aqueous solution by extraction and spectrophotometric examination of the extract at 392.5 mμ.

Gallium dibromoxinate (5,7-dibromo-8-hydroxyquinolate), $Ga(C_9H_4Br_2NO)_3$, was prepared (1) and chloroform solutions were examined spectrophotometrically in the region 249-800 mμ. Four absorption peaks were observed at 268.5, 331, 344 and 410 mμ. The 410 mμ peak was found to obey Beer's Law and be suitable for the determination of traces of gallium in aluminum ores. The lower and upper limits of the colorimetric determination were found to be 0.062 and 1.00 mg. of gallium (as the metal) per liter of chloroform, respectively.

Gallium dichloroxinate (5,7-dichloro-8-hydroxyquinolate),

was prepared, for the first time, in a manner similar to that used for the preparation of the corresponding dibromoxinate. The formula was found to be $Ga(C_9H_4Cl_2NO)_3$, and the precipitation was quantitative. The absorption spectrum in chloroform solution was found to be similar to that of the corresponding dibromoxinate.

Chloroform solutions of aluminum oxinate and dibromoxinate were examined spectrophotometrically and the absorption spectra were found to be closely similar to those of the corresponding gallium compounds.

A solution of indium oxinate, $In(C_9H_6NO)_3$, in chloroform was examined by means of the spectrophotometer in the wave length region 295-500 mμ. Characteristic absorption peaks were observed at 320, 336 and 395 mμ.

Chloroform solutions of thallium(I) oxinate, $Tl(C_9H_6NO)$, prepared by the method of Rey (4), were examined spectrophotometrically in the region 300-1000 mμ. Although the solutions of this compound were found to be both thermally and photochemically active, the absorption spectra could be observed if solutions were prepared in the darkroom and observed immediately. Characteristic absorption peaks were observed at 310, 325, 338 and 395 mμ. The last peak was found to obey Beer's Law.

Thallium(III) oxinate, $Tl(C_9H_6NO)_3$, was prepared by essentially the same precipitation procedure as that used for the gallium compound, except precipitation and digestion were carried out at room temperature. The first permanent precipitate appeared at a pH of 3.0, and precipitation was complete at pH 3.7-3.8. This compound appears suitable as a means of determining thallium gravimetrically, as shown by seventeen determinations on known solutions containing from 1.0 to 200.0 mg. of thallium. In the range 300-1000 mμ, three absorption peaks were observed at 328, 338 and 400-402 mμ for chloroform solutions of thallium(III) oxinate. The 400-402 mμ peak was found to adhere closely to Beer's Law in the concentration range 0.2-8.0 mg. of thallium (as the metal)

per liter of solvent. Chloroform solutions of this compound are much less stable in sunlight than those of gallium and indium. Solutions prepared in the darkroom and protected from light may be used for colorimetric determination of thallium. In acetate-buffered solutions, thallium(III) did not precipitate until a pH of 7.0 was reached, while in sulfuric acid solutions it precipitated at about a pH of 1.0. In acetate-buffered solutions, maximum extraction of thallium(III) by means of oxine in chloroform occurred in the narrow pH interval of 6.5-7.0. The extraction was not quantitative.

The absorption spectra of solutions of quinoline, oxine, dichloroxine and dibromoxine in chloroform were observed and compared. The absorption peaks of the IIIB family oxinates were compared and relationships established.

Summary

The chemistry and the absorption spectra of the IIIB family oxinates are closely similar. Trends in the subfamily were found in respect to the pH of oxinate precipitation, the pH of oxide precipitation and the incident pH of maximum extraction of oxinate into chloroform. Regular shifts in the wave lengths of absorption spectra peaks to higher values were observed from aluminum through thallium. The molecular extinctions of the most characteristic peaks of the IIIB family oxinates were found to be nearly equal and to adhere to Beer's Law. The oxinates of gallium and thallium(III) as well as aluminum and indium are applicable to analytical practice. There is a definite subjugation of the metallic properties of the elements to the covalent organic properties of the quinoline derivative chelated to them.

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VITA

The author was born July 21, 1918, in Louisville, Kentucky. He attended public schools in St. Petersburg, Florida and was graduated from St. Petersburg Senior High School in June, 1936. In September of the same year, he entered the University of Florida and received the degree of Bachelor of Science with a major in chemistry in June, 1940. He was awarded a Board of Control Graduate Scholarship at the University of Florida for the year 1940-41. In July, 1941, he was employed as an analytical chemist by the Tennessee Valley Authority at Wilson Dam, Alabama. In January, 1942, he was employed as a physicist in closed bomb ballistics at the Indiana Ordnance Works, Charlestown, Indiana. He volunteered for duty in the Navy and was commissioned an Ensign in February, 1943. He was called to active duty on May 1, 1943 and served thirty-three months, eighteen months being sea duty in the Atlantic and European-African theatres. He was released to inactive duty with the rank of Lieutenant on January 29, 1946. He entered Purdue University in March, 1946, and held a graduate assistantship while in attendance. At the end of the summer of 1947, he left Purdue to continue his studies at the University of Illinois. He has held a half-time research assistantship sponsored by the Office of Naval Research while at Illinois.

The author is a member of the American Chemical Society, Gamma Sigma Epsilon, Phi Eta Sigma, Phi Lambda Upsilon, Sigma Xi, and a Naval Research Reserve Unit.

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